

KINETICS OF IONIZATION OF ACETALDEHYDE*

By P. T. McTIGUE,† J. KIRSANOV,† and H. TANKEY†

Owing to the ease with which aldehydes are oxidized by halogens it has proved impossible to follow the base-catalysed enolization of aldehydes possessing α -halogens by measuring the rate of zero-order halogenation, which is the usual technique applied to ketones. A reaction whose rate appears to be controlled by the ionization rate of acetaldehyde is the condensation between formaldehyde and acetaldehyde, which ultimately yields pentaerythritol. This has a rate law:

$$-d[A]/dt = k_e[A][OH^-] \quad (1)$$

where A represents acetaldehyde and OH^- the hydroxide ion. The reaction is thus zero-order with respect to formaldehyde. Some preliminary measurements¹ of the rate of this reaction have been reported, and the present work provides more complete data. In particular the hydroxide ion concentrations have been determined with an alkali-sensitive glass electrode and a pH meter. We believe this procedure is more satisfactory than that used previously when hydroxide ion concentrations were calculated using the known pK_a of formaldehyde hydrate, together with an estimate of the degree of polymerization of the formaldehyde in the solutions used.

Experimental

Inorganic chemicals were all of A.R. grade. Acetaldehyde was B.D.H. laboratory reagent, distilled in a current of nitrogen. Formaldehyde was supplied by B.D.H. as a 40% aqueous solution. Acetaldehyde solutions were made up by weight and formaldehyde was determined as previously described. The dilatometer used was similar to those previously described. Spectrophotometric work was carried out with a Hilger Uvispek spectrophotometer with an electrically heated cell block held at $25 \pm 0.1^\circ$. pH measurements were made with an E.I.L. direct reading pH meter.

Results

As previously reported¹ the reaction may be followed dilatometrically, and the initial reaction rate can be expressed as a dilatometric rate in sec^{-1} . Twelve runs were carried out and it was shown that the rate law (1) was obeyed in the following concentration ranges:

$$\begin{aligned} 3 \times 10^{-4}M &\leq [OH^-] &< 6 \times 10^{-3}M \\ 0.45M &\leq [HCHO] &< 3.5M \\ 0.05M &\leq [CH_3CHO] &< 0.20M \end{aligned}$$

An ultraviolet spectroscopic investigation of the reaction confirmed that the carbonyl absorption band at $280 \text{ m}\mu$ steadily disappeared during the course of the reaction,

* Manuscript received December 10, 1963.

† Department of Physical Chemistry, University of Melbourne.

¹ Bell, R. P., and McTigue, P. T., *J. Chem. Soc.* 1960, 2983.

and the initial rate of optical density decrease could be used as a direct measure of the initial reaction rate, by means of the known extinction coefficient (7.7) of acetaldehyde in aqueous solutions at 25°. Using concentrations in the ranges quoted above, five runs gave an average value:

$$k_e = 0.15 \pm 0.01 \text{ l. mole}^{-1}\text{sec}^{-1},$$

for the hydroxide-ion catalysed enolization of acetaldehyde. This compares with the value of $0.09 \text{ l. mole}^{-1}\text{sec}^{-1}$ given by Bell and McTigue¹ for the same quantity. The latter value is probably less reliable since it depends on a detailed knowledge of the polymerization equilibria in concentrated formalin. Such data are not available.